The Activity of Carbon Activated by Ammonia Gas*

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The activity of powdered charcoal activated by ammonia gas was evaluated from the rate constant of hydrogen peroxide decomposition, rate of oxygen adsorption, BET surface area, adsorption amount of diphenylguanidine or benzoic acid, wettability, and pore size distribution curves. In order to examine the electrochemical property of the activated carbon, polarization curves were measured. The main conclusion to be drawn from these experimental results is as follows. The surface area of carbon samples was proportional to weight loss under condition of a fixed activating temperature. The rate constant of hydrogen peroxide decomposition and the adsorption amounts of diphenylguanidine and benzoic acid increased with increasing the surface area of the carbon samples under condition of the fixed temperature. The surface property such as wettability was influenced by the activating temperature. From the pore size distribution curves of carbon samples, it was recognized that the micro-pore having the size below 100Å was developed by the activation treatment. The carbon electrode treated with ammonia was excellent in a polarization curve as an air-carbon electrode.

1 Introduction

In general, a porous carbon electrode is non-active in acids and in bases and also one of excellent catalytic carriers which could be modified its porosity and pore size. Therefore, the porous carbon electrode has been widely used as the electrode of air cells, hydrogen-oxygen fuel cells, and others.

As part of the investigation of the porous carbon electrodes[1)-5)] the activities of powdered carbon activated by ammonia gas were evaluated from the rate constant of hydrogen peroxide decomposition, rate of oxygen adsorption, BET surface area, and adsorption amount of diphenylguanidine or benzoic acid. The adsorption isotherm experiments of water vapor and nitrogen were made for the purpose of examining wettability and pore size distribution curves respectively.

2 Experimental

2. 1 Sample preparation

Powdered carbon of 60–100 meshes range was prepared by grinding charcoal. Carbon treated with ammonia gas is known to become active electrochemically.[6)-8)] From the above standpoint the activation by ammonia gas was carried out using the vessel

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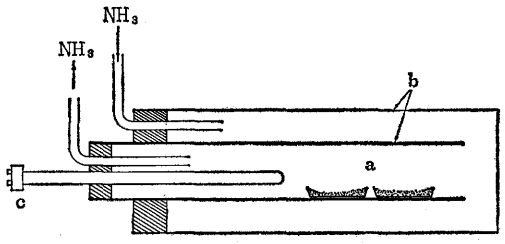
designed with quartz as shown in Fig. 1. After the powdered carbon, 2g, put into a porcelain boat was heated upto the prescribed temperature in an atmosphere of nitrogen, it was heated for 45–465 minutes under the condition of the ammonia gas flow rate of 500 ml/min or 1000 ml/min. The powdered carbon obtained was kept in a desiccator.



a: Powdered carbon b: Quartz tube c: Thermocouple

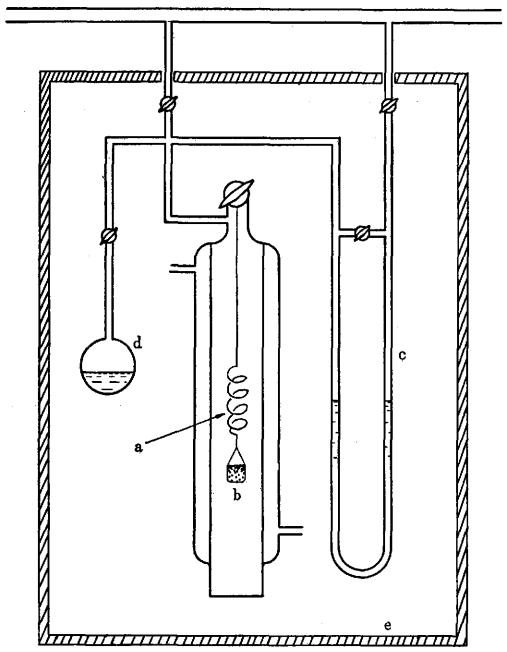
Fig. 1 Vessel for activating by NH_3

2. 2 Measurements of nitrogen adsorption isotherms

Nitrogen adsorption isotherms were measured by the BET apparatus. Exactly the 0.1g of the carbon sample was put into a cell and then it was degassed at 300°C for 3 hours under the condition of 10^{-5}mmHg. Adsorption equilibrium time was determined from the preliminary experiments. Surface area and pore size distribution curves of the carbon samples were determined from the adsorption isotherms obtained.

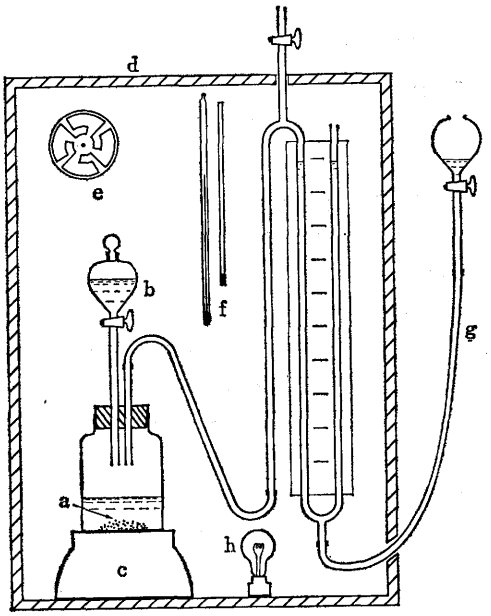
2. 3 Measurements of water vapor adsorption isotherms

This experiment was undertaken to examine the wettability of the carbon samples.[3),6)] The apparatus with spring balance made of quartz is shown in Fig. 2. Its sensitivity is 21mg/mm. Exactly the 0.5g of the sample was put into a quartz cell (15ϕ×10) and



a: Quartz spring b: Sample c: Manometer
d: Water e: Thermostat

Fig. 2 Apparatus for measuring water vapor adsorption



a: Sample b: H_2O_2 c: Magnetic stirrer d: Thermostat
e: Fan f: Thermometer g: Gas burette h: Heater

Fig. 3 Apparatus for measuring rate cnstant of H_2O_2 decomposition

it was then degassed under the condition of 10^{-5}mmHg. Adsorption amount of water vapor at equilibrium was determined from change in weight under the constant water vapor pressure. The temperature of an air bath was maintained at 30°C all through the experiment.

2. 4 Rate constant of hydrogen peroxide decomposition

Fig. 3 shows the designed apparatus for measuring the rate constant of hydrogen peroxide decomposition. The experimental procedure is as follows. Constant volume of 0.3% H_2O_2 solution was added to a glass bottle containing 0.3g carbon. Amount of evolved oxygen was measured with a gas burette. Being proportional to weight of the carbon sample added to the solution, the rate constant was calculated as the value per gram carbon. Temperature was kept constant at 30°C by using an air bath.

2. 5 Adsorption of diphenylguanidine and benzoic acid

The adsorption equilibria of diphenylguanidine and benzoic acid were measured for the purpose of determining acidic and basic functional groups. The carbon sample of 0.5g was immersed in 0.01N ethanol solution, 50ml, of diphenylguanidine or benzoic acid at 30°C for 3 days. After the carbon filterating, pH titration was carried out with 0.01N HCl or NaOH solution. Amount of the adsorption was determined from the difference between above titration and blank test.

2. 6 Measurement of oxygen adsorption rate

Oxygen adsorption rate of carbon sample is important factor for the oxygen-carbon electrde reaction.[9),10)] From a reason of this, the experiment was carried out by using BET apparatus under oxygen pressure of 30mmHg. Amount of oxygen adsorption at equilibrium was determined from change in volume of oxygen under same oxygen pressure. Oxygen adsorption rate of carbon sample was calculated from data of the adsorption amount and equilibrium time. Temperature was kept constant at 0°C by using a mixture of water and ice.

3 Results and Discussion

Table 1 shows the characteristics of powdered charcoal activated by ammonia gas. On the basis of data in Table 1, a relation between surface area and weight loss is plotted in Fig. 4. The surface area increases with weight loss. Fig. 5 illustrates a relation between the rate constant of hydrogen peroxide decomposition and the surface area. The rate constant increases with increasing surface area. On the basis of results in Fig. 4 and 5, it seemed reasonable to assume that the activation mechanism of carbon with ammonia is similar in the case of the treating temperature at 800 or 900°C. The rate of reaction at 800°C, however, considerably slow. On the other hand, the mechanism in the case of 1000°C is distinguishable from those in other temperatures. The increase of the surface area suggests that the activation treatment by ammonia increases the roughness and open pores on the carbon surface. The increase of the rate constant of hydrogen peroxide decomposition would result in a

Table 1 The characteristics of powdered charcoal activated by ammonia

Designation	Treating Temperature (°C)	Activating time (min)	Weight loss (%)	Surface area (m^2/g)	H_2O_2 decomposition rate constant ($10^{-8} \cdot sec^{-1}$)	O_2 adsorption rate (ml/min • g)	DPG*1 adsorption (10^{-4}mol/g)	BA*2 adsorption (10^{-4}mol/g)
1	—	—	—	313	0.11	0.31	0.00	0.00
2	500	120	3.8	369	0.25	0.38	0.01	0.52
3	700	120	10.5	411	0.61	0.97	0.48	1.44
4	800	120	15.5	489	0.87	1.09	1.39	2.20
5	800	150	18.1	498	4.6	—	1.32	3.70
6	800	300	30.9	725	14.5	—	2.68	4.90
7	800	450	42.4	889	26.4	—	2.96	5.28
8	800	465	47.3	961	26.0	—	2.87	5.62
9	900	45	18.1	486	4.4	—	0.97	3.30
10	900	120	18.8	531	5.0	1.75	1.77	3.50
11	900	60	23.6	524	6.8	—	2.44	4.38
12	900	90	26.4	684	8.9	—	3.02	4.92
13	900	240	41.0	866	28.8	—	3.81	4.97
14	900	180	48.3	1,171	30.0	—	3.93	5.41
15	1,000	120	21.7	549	2.4	1.28	2.74	3.10
16	1,000	90	28.2	410	4.2	—	1.79	2.35
17	1,000	135	37.9	648	3.1	—	2.56	2.64
18	1,000	155	48.7	814	5.1	—	3.03	3.46

*1 DPG : Diphenylguanidine *2 BA : Benzoic acid

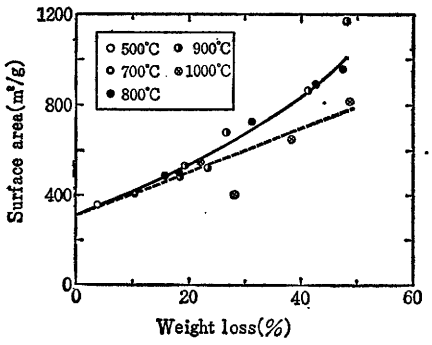


Fig. 4 Relation between surface area and weight loss

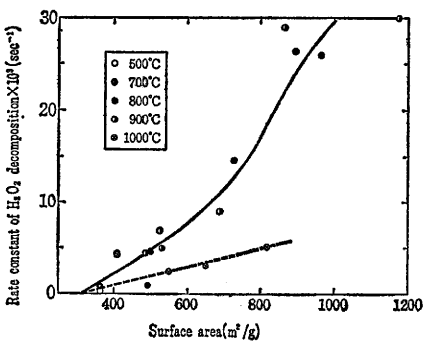


Fig. 5 Relation between rate constant of H_2O_2 decomposition and surface area

greater number of active points and fields of the electrochemical reaction as a carbon electrode and, consequently, the electrode performance can be shown great promise.

As shown in Table 1, the rate of oxygen adsorption onto carbon surface was accelerated in the range of 800 to 900°C under conditions of 500ml-NH_3/min and treating time of 120 minutes. This fact is similar in result of the rate constant of hydrogen peroxide decomposition. In order to discuss the above fact, further, a relation between the rate constant of hydrogen peroxide decomposition and the rate of oxygen adsorption is plotted in Fig. 6. As shown in Fig. 6, the rate constant of hydrogen peroxide decomposition is proportional to the rate of oxygen adsorption. The rate constant of

hydrogen peroxide decomposition increases remarkably after about 1.0 ml/min/g. It is thought that this fact results from difference in the surface property owing to the formation of some surface active compounds on carbon treated with ammonia gas.

Water vapor adsorption isotherms are shown in Fig. 7. In the range of 500 to 800 °C, the amount of water vapor adsorption increased with raising temperature. That is to say, wettability of the carbon sample increased gradually with treating temperature. On the other hand, water vapor adsorption isotherms of the carbon sample treated at 900 or 1000°C shifted to higher relative pressure than the others. This fact suggests that the carbon treated with ammonia at 900 or 1000°C has hydrophobic surface property relatively. In order to determine the surface functional groups of sample carbon, the adsorption amounts of diphenylguanidine and benzoic acid were determined. The results obtained, together with other properties, are given in Table 1. The acidic and basic surface compounds on the carbon sample increased with treating temperature under the condition of fixed treating time. It seems that the activity of the carbon sample treated at 900°C, particularly, is superior to others by cosidering the data of the rate constant of hydrogen peroxide decomposition and oxygen adsorption rate. In order to consider the above data, the carbon samples, which are different in weight loss, were further prepared by changing the treating time at constant temperature. The adsorption amounts of diphenylguanidine and benzoic acid of the carbon samples treated at 800 or 900°C increased with the weight loss. These adsorption amounts are closely related to the rate constant of hydrogen peroxide decomposition. On the other hand, the adsorption amount of

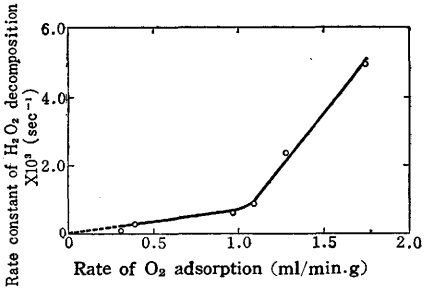


Fig. 6 Relation between rate constant of H_2O_2 decomposition and rate of O_2 adsorption

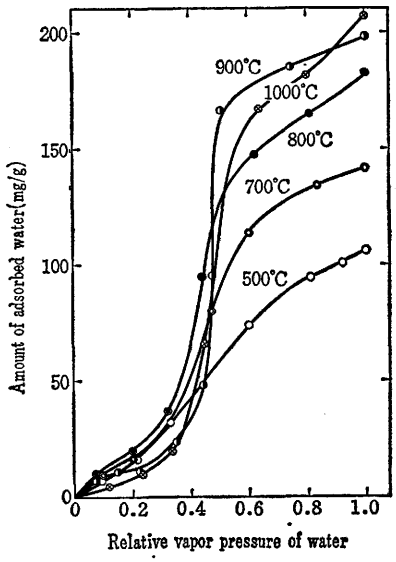


Fig. 7 Water vapor adsorption isotherms

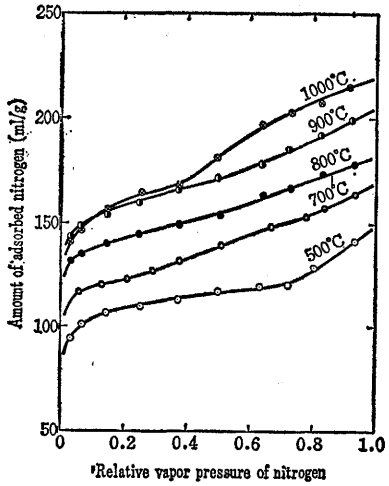


Fig. 8 Nitrogen adsorption isotherms

the carbon sample treated at 1000°C was less than the others in spite of increasing the weight loss. Therefore, it seems that the rate constant of hydrogen peroxide decomposition was also little. On the basis of these data, it seemed reasonable to assume that the optimum treating temperature is the range of 800 to 900°C. This agreed with the results obtained by another investigator.[6] Nitrogen adsorption isotherms of carbon treated with ammonia at various temperatures are shown in Fig. 8. On the basis of the data shown in Fig. 8, the pore size distribution curves were determined by Inkley's method.[3] According to this method, the pore volume having radius of r_1–r_2 is expressed as the following equation.

$$V_{12}=R_{12}\left(v_{12}-k_{12}\sum_{d_2+1/2\Delta d}^{d_{max}}\frac{d-2t_{12}}{d^2}V_d\Delta d\right) \qquad \cdots\cdots\cdots(1)$$

Where

$$R_{12}=\frac{r_2-r_1}{\int_{r_1}^{r_2}[(r-t_1)^2/r^2]dr}$$

$$k_{12}=4(t_2-t_1)$$

$$t_{12}=1/2(t_1+t_2)$$

Also, v is the adsorption amount, t is the thickness of adsorbed layer, r is the pore radius, and d is the pore diameter. Pore size distribution curves were obtained by plotting $V_{12}/\Delta d$ vs. d. The results obtained were illustrated in Fig. 9. From Fig. 9, it was recognized that the micropore having pore size below 100 Å developed with the treating temperature. In comparison with peaks of pore diameter those shifted to large value with elevating temperature. This suggests that as the activation reaction by ammonia proceeds, the closed pore of the carbon sample changes into the open pore, or the pore of ink bottle disappears gradually.

In order to investigate the electrochemical property of the activated carbon, porous carbon electrodes were prepared from powdered charcoal, graphite, and sawdust. The binder was the mixtures of pitch and coaltar with a ratio of 1 : 3. The apparatus

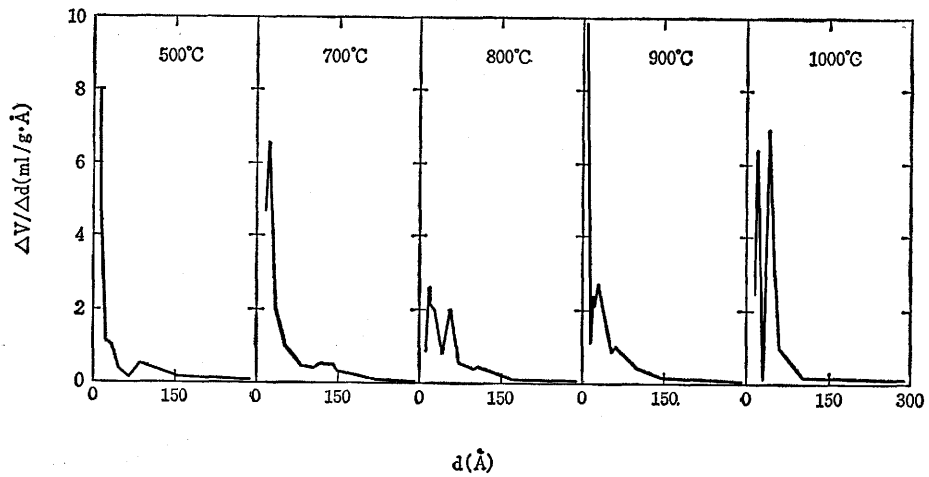
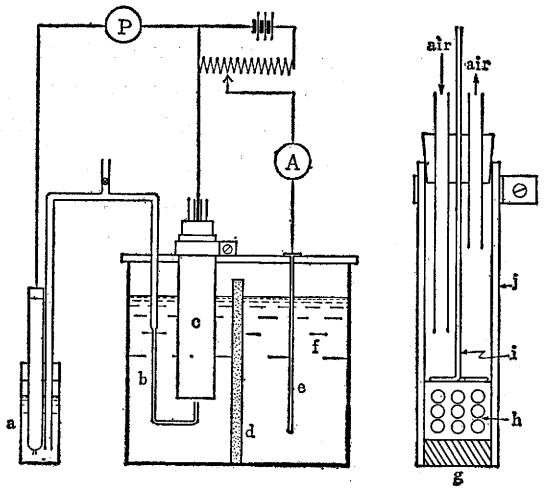


Fig. 9 Pore size distribution curves of NH_3 activated carbons at various temperatures for 2 hours



A : Ammeter
P : Potentiometer
a : HgO/Hg reference electrode
b : Luggian capillary
c : Air-carbon electrode
d : Diaphragm
e : Counter electrode (Ni)
f : 30% KOH
g : Carbon electrode
h : Graphite
i : Cu wire
j : Plastic pipe

Fig. 10 Apparatus for measuring polarization

for polarization measurement and the construction of an air-carbon electrode are given in Fig. 10. The details of experimental procedure are as follows. A 30%-KOH solution was selected as a medium electrolyte and nickel was used as a counter electrode. The air-carbon electrode was compulsively polarized by an external battery. The air-carbon electrode potential vs. HgO reference electrode was measured by a potentiometer at 30°C. The polarization curves obtained are shown in Fig. 11. The electrochemical reduction of oxygen according to the overall reaction scheme

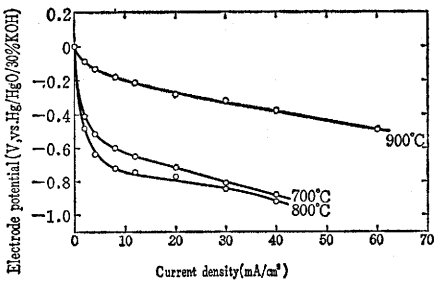


Fig. 11 Polarization curves of air-carbon electrodes treated with NH_3

$$1/2O_2+H_2O+2e=2OH^- \qquad \cdots\cdots(2)$$

involves a number of theoretical as well as practical problems.

The reaction mechanism in an alkaline medium can be expressed by the following equations.[9),11)]

$$O_2 \longrightarrow O_{2ad} \qquad \cdots\cdots(3)$$

$$O_{2ad}+H_2O+2e=HO_2^-+OH^- \qquad \cdots\cdots(4)$$

$$HO_2^-+OH^- \longrightarrow 2OH^-+1/2O_2 \qquad \cdots\cdots(5)$$

As shown in Fig. 11, the polarization curve of the carbon electrode treated with ammonia at 900°C is superior to others. In cosideration of these results and data of the rate constant of hydrogen peroxide decomposition and the rate of oxygen adsorption, it is reasoned that the carbon electrode treated at 900°C accelerates the rate determining reactions, that is equation 2 and 4.

4 Conclusion

The activity of powdered charcoal activated by ammonia gas was evaluated from the rate constant of hydrogen peroxide decomposition, rate of oxygen adsorption, B.E.T.-surface area, amount of diphenylguanidine or benzoic acid adsorption, wettability, and pore size distribution curves. In order to examine the electrochemical property of the activated carbon, polarization curves were measured. The main conclusion to be drawn from these results is as follows. The surface area of carbon samples was proportional to weight loss under condition of a fixed activating temperature. The rate constant of hydrogen peroxide decomposition and the adsorption amounts of diphenylguanidine and benzoic acid increased with increasing the surface area of the carbon samples under condition of the fixed temperature. The surface property such as wettability was influenced by the activating temperature. From the pore size distribution curves of carbon samples, it was recognized that the micro-pore having size below 100Å was developed by the activation treatment. The carbon electrode treated with ammonia was excellent in a polarization curve as an air-carbon electrode.

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